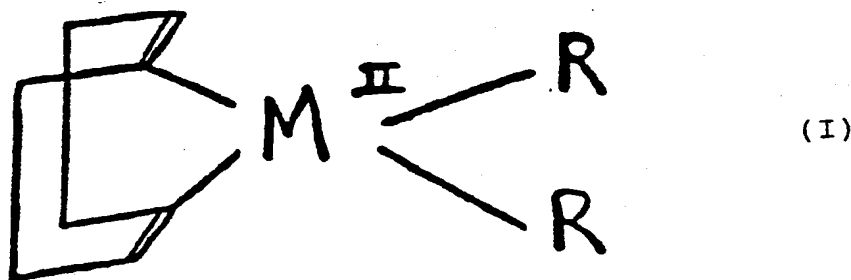


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**(54) Title: FUEL ADDITIVES AND FUEL CONTAINING SOLUBLE PLATINUM GROUP METAL COMPOUNDS AND USE IN INTERNAL COMBUSITON ENGINES**



A gasoline and diesel fuel additive composition comprising solutions of a fuel-soluble platinum group metal compound in a solvent miscible in the diesel, the platinum group metal complex being present in an amount sufficient to supply from 0.01 to 1.0 parts per million of the platinum group metal when added to a predetermined amount of fuel. Preferred solvents are oxygenated hydrocarbons such as ethanol, tetrahydrofuran, and methyl tertiary butyl ether, and will preferably be employed in amounts of less than 5% of the weight of the gasoline to provide oxygen and the metal at a weight ratio of from 1,000:1 to 100,000:1. Especially preferred compounds are those of formula (I), wherein M is a platinum group metal and R is benzyl, phenyl or nitrobenzyl. The additive compositions and fuel treated therewith improve operating efficiency of internal combustion engines in terms of increased power output per unit of fuel burned and reduce the emissions of particulates and noxious gases such as carbon monoxide and nitrogen monoxide. The additives provide beneficial results upon immediate use and over long periods of continuous use.

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DESCRIPTION

FUEL ADDITIVES AND FUEL CONTAINING SOLUBLE  
PLATINUM GROUP METAL COMPOUNDS AND  
USE IN INTERNAL COMBUSTION ENGINES

5 Related Applications

This application is a continuation-in-part of  
commonly assigned co-pending patent applications  
Serial No. 677,954, filed on 4 December 1984, and  
U.S. Serial No. 790,738, filed on October 24, 1985,  
10 both by Bowers and Sprague, the inventors herein.

Technical Field

The present invention relates to improving the  
performance of internal combustion engines, both  
gasoline and diesel; and, more particularly, to the  
15 formulation and use of fuel additives and fuels  
which burn more efficiently and with reduced noxious  
emissions.

Background Art

Prior investigations involving the use of  
20 platinum group metals in internal combustion engines  
have led to the development of the catalytic  
converter for emissions reduction. Reliance upon  
costly mechanical equipment, while less than ideal

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or desirable, has become standard despite the efforts of the prior art to accomplish the same result through less costly combustion improvements in terms of better combustion conditions through engine design and fuel additives. The efforts in engine design have provided significant improvements, but the twin objectives of improved operating efficiency and reduced noxious emissions are difficult to achieve simultaneously.

Experience to date with fuel additives has been less successful, due in part to the complicated equipment necessitated for their introduction into the fuel supply and in part to their cost where they include more exotic catalytic materials. For example, in U.S. Patent 4,295,816, Robinson discloses an elaborate delivery system for introducing water-soluble platinum group metal salts through the air intake of internal combustion engines to deliver platinum group metal catalysts to the combustion chamber at a level no greater than 9 mg catalyst per kilogram of fuel.

In U.S. Patents 2,086,775 and 2,151,432, Lyons and McKone disclose adding from 0.001 to 0.085% (i.e., from 10 to 850 parts per million) of an organometallic compound or mixture to a base fuel such as gasoline, benzene, fuel oil, kerosene, or blends to improve various aspects of engine performance. Among the metals disclosed in U.S. 2,086,775 are cobalt, nickel, manganese, iron, copper, uranium, molybdenum, vanadium, zirconium, beryllium, platinum, palladium, chromium, aluminum, thorium and the rare earth metals, such as cerium.

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Among those disclosed in U.S. 2,151,432 are selenium, antimony, arsenic, bismuth, cadmium, tellurium, thallium, tin, barium, boron, cesium, didymium, lanthanum, potassium, sodium, tantalum, titanium, tungsten and zinc. In both disclosures, the preferred organometallic compounds were beta diketone derivatives and their homologues, such as the metal acetylacetonates,, propionylacetonates, formylacetonates, and the like. Such compounds typically provide oxygen-to-metal ratios in the range of 1:1 to 1:10, and no essential feature linked to the presence of oxygen is disclosed.

The Lyons and McKone disclosures state that concentrations of from 0.001 to 0.04% (i.e., from 10 to 400 parts per million) are not effective to improve combustion efficiency as introduced, but may become so upon prolonged use as catalytically active deposits are built up in the combustion chamber. The disclosure further states that about 0.01% (i.e., 100 ppm) of the organometallic compound is usually sufficient, once the requisite amount of catalytically active deposits has been built up, to perpetuate that amount of deposits by replacement of losses therefrom. The compounds disclosed were, therefore, not capable of generating any instantaneous catalytic effect at low concentrations. U.S. Patent 2,460,780 to Lyons and Dempsey, which relates principally to water-soluble catalysts, confirms this at column 1, lines 11-36. Further, no indication was made for preferred oxidation states for the metals disclosed.

Neither of the Lyons and McKone patents disclose the use of oxygenated solvents or point to the importance of high oxygen to metal ratios. In Demonstration 15 in U.S. Patent 2,086,775, palladium

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acetylacetonate was added to a fuel (not specifically identified, but presumably the leaded 65 octane gasoline employed in Demonstration 1) at a level of 0.002% (20 ppm). The weight ratio of oxygen to palladium was not mentioned, although by calculation it is found to be about 1 to 3, and the level of palladium is found to be about 10 ppm. No improvement in combustion was noted until after substantial driving.

10       The above-noted U.S. Patent 2,460,780 to Lyons and Dempsey relates principally to employing catalysts which are soluble in water or other "internal liquid coolants" such as alcohol, water-soluble glycols or aqueous solutions of these.

15       While catalyst levels based on the weight of metal compounds as low as 0.001% are disclosed, it is stated that for immediate catalytic effect the catalyst compounds for useful effect may be present at a level of at least 1% of the weight of the

20       operating fuel charge. In some Examples, fuel-soluble cobalt, cerium and chromium catalysts are added to the fuel at total catalyst levels of 0.01%. No disclosure is given of fuel-soluble catalysts at levels below 0.01% or with oxygenated solvents.

25       Moreover, where alcohol and glycols are employed with water-soluble catalysts, they are disclosed principally as solubilizing carriers for the catalysts and for their known internal cooling function at high load.

30       In German Offenlegungsschrift 2,500,683, Brantl discloses that a wide variety of catalytic metals may be added to hydrocarbon fuels to reduce nitrogen monoxide and oxidize carbon monoxide at the moment of combustion in internal combustion engines. The

35       disclosure states that organometallic or Grignard

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compounds of the metals lithium, sodium, lead, beryllium, magnesium, aluminum, gallium, zinc, cadmium, tellurium, selenium, silicon, boron, germanium, antimony and/or tin can be added to the  
5 fuel individually or as a mixture. Similarly, the metal complexes of the metals scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, ruthenium, rhodium, palladium, osmium, iridium, platinum, silver, gold, gallium,  
10 molybdenum, lead and mercury, with different ligands, can be added to the fuel individually or as a mixture. For the platinum group metals osmium, iridium, and platinum, broad concentrations of from 0.347 to 3.123 grams per liter of fuel are suggested  
15 for the various compositions listed in the disclosure, with the range for particularly favorable results being from 0.868 to 1.735 grams per liter of fuel. Considering the cost of these metals and the compositions containing them, there  
20 is a negative incentive for employing them at the high levels stated by the disclosure to be effective. Moreover, the tetramethyl platinum compound is not known to exist.

In U.S. Patent 2,402,427, Miller and Lieber  
25 disclose the use of certain diesel-fuel-soluble organic or organometallic compounds as ignition promoters at concentrations of from 0.02 to 3% (i.e., 200 to 30,000 parts per million). No platinum group metal compounds are identified and no  
30 indication is given that the disclosed compounds at the disclosed or lower levels would improve combustion in a gasoline internal combustion engine.

Other work done, in which cylinders of a diesel engine were coated with platinum metal, showed  
35 reductions in noxious emissions, but the coating wore off in a number of hours.

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Disclosure of Invention

The present invention comprises the application of certain platinum group metal compounds which are directly soluble in engine fuels, such as diesel fuel or gasoline, or solvents for use in internal combustion gasoline and diesel engines. The compounds, preferably in combination with a solvent for them which is also miscible in the fuel, are employed at very small, but catalytically effective levels of from 0.01 to about 1.0 parts of platinum group metal per one million parts of fuel (ppm). For the purposes of this description, all part per million figures are on a weight to volume basis, i.e., mg/liter, and percentages are given by weight, unless otherwise indicated.

According to one its aspects, the invention provides gasoline and diesel fuel additive compositions comprising a solution of a fuel-soluble platinum group metal compound in a solvent miscible in the fuel, the platinum group metal compound being present in an amount sufficient to supply from 0.01 to 1.0 parts per million of the platinum group metal when added to a predetermined amount of fuel.

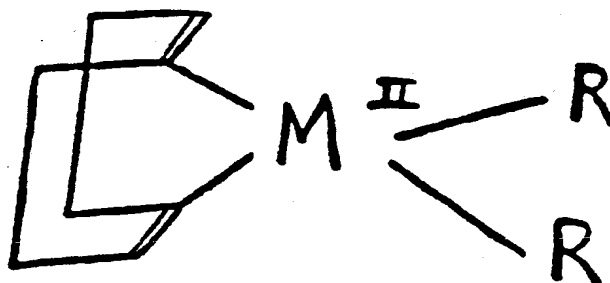
Preferred solvents are oxygenated hydrocarbons such as ethanol, tetrahydrofuran, and methyl tertiary butyl ether, and will preferably be employed in amounts of less than 5% of the weight of the fuel. The oxygenated solvents will preferably be employed in amounts sufficient to supply oxygen at a weight ratio to the platinum group metal of at least 1000:1.

Among the preferred platinum group metal compounds are platinum group metal coordination compounds comprising a platinum group metal having a



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+2 or +4 coordination state with at least one coordination site in the compound being occupied by a functional group containing at least one unsaturated carbon-to-carbon bond with an olefinic, acetylenic or aromatic pi bond configuration. Especially preferred compounds are those of the formula:



wherein M is a platinum group metal and R is benzyl, phenyl or nitrobenzyl.

10 According to another aspect of the invention, gasoline and diesel fuel compositions of improved properties are provided, which comprises gasoline or diesel fuel and an additive composition dissolved therein, said additive composition comprising a  
15 fuel-soluble platinum group metal compound in an amount effective to supply from 0.01 to 1.0 parts of the platinum group metal per million parts of fuel.

According to a further aspect of the present invention, there is provided a method of increasing  
20 the utilizable energy of gasoline or diesel fuel for powering internal combustion engines, comprising admixing with said gasoline or diesel fuel an additive composition comprising a fuel-soluble platinum group metal compound in an amount effective  
25 to supply from 0.01 to 1.0 parts of the platinum group metal per million parts of fuel.

The additive compositions according to the invention improve operating efficiency of gasoline

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and diesel internal combustion engines in terms of increased power output per unit of gasoline burned and reduce the emissions of particulates and noxious gases such as carbon monoxide and nitrogen monoxide.

5 The additives provide beneficial results upon immediate use and over long periods of continuous use.

For the purposes of this description, gasoline is defined as a mixture of volatile hydrocarbons for  
10 use in a spark-ignited internal combustion engine and having an octane rating  $[(\text{Research} + \text{Motor})/2]$  of at least 80, typically about 87 to 89 or above, and according to the more preferred aspects of the invention as having less than 1.4 grams per gallon  
15 of lead. Most preferably, the gasoline will be "unleaded" and contain no more than 0.05 grams of lead per gallon and no more than 0.1% of sulfur. Gasoline typically has a BTU value of about 19,700 calories per pound.

20 The gasoline additive compositions of this invention achieve the most reproducible effect in engines operated under lean conditions, namely an air to fuel ratio of about 14.7:1, and at compression ratios from about 7:1 to 9:1.

25 Diesel fuels, for the purposes of this description, are defined as fuel oil number 2 petroleum distillates of volatility and cetane number characteristics effective for the purpose of fueling internal combustion diesel engines.

30 As indicated above, the preferred platinum group metal compounds are coordination compounds. These compounds, especially those coordinated with certain high molecular weight (preferably above 100 daltons) olefinic functional groups, are stable in

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the presence of moisture. This is extremely important due to the amounts of water present in gasoline and diesel fuels. Gasoline, for example, will typically contain dissolved water in amounts on the order of 30 ppm and frequently contains higher levels of dispersed and bulk water.

Few, if any, platinum group metal coordination compounds which are directly soluble in gasoline or diesel fuel are available commercially. Compounds which are available often contain objectionable functional groups containing halogen and phosphorus and, therefore, are less than preferred for many internal combustion applications. Preferably, the compounds according to the present invention will have no phosphorus or have low levels which are free of significant disadvantages. We have discovered that certain platinum group metal compounds can be prepared which are soluble and stable in the fuels and actively catalyze the combustion of gasoline and diesel fuel in internal combustion engines and reduce noxious emissions when introduced as an integral part of the fuel.

The preferred class of materials used include platinum group metal coordination states II and IV. Compounds in the lower (II) state of oxidation are preferred due to their function in generating the catalytic effect. A significant feature of the invention is the use of platinum group metal II coordination compound having at least one coordination site occupied by a functional group containing an unsaturated carbon-to-carbon bond of the olefinic, acetylenic or aromatic pi bond configuration. Preferably, two or more of the coordination sites will be occupied by such functional groups since the stability and solubility

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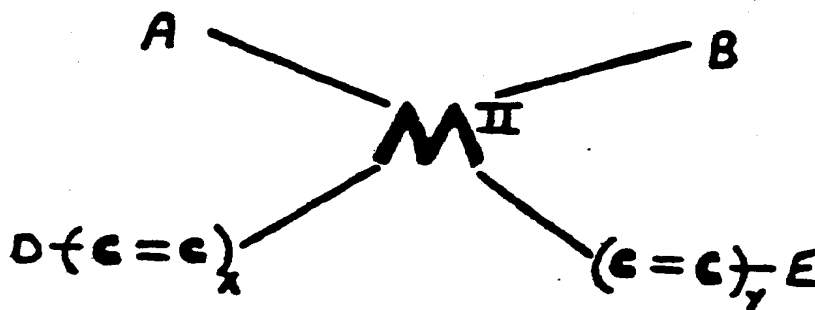
in gasoline and diesel fuel of compounds having such multiple functional groups are improved. While wishing not to be bound to any particular theory, it is believed that such preferred compounds in the lowest possible oxidant state are the most beneficial for producing instantaneous catalytic effect.

Occupation of one or more coordination sites with the following unsaturated functional groups have been found useful:

1. Benzene and analogous aromatic compounds such as anthracene and naphthalene.
2. Cyclic dienes and homologues such as cyclooctadiene, methyl cyclopentadiene, and cyclohexadiene.
3. Olefins such as nonene, dodecene, and polyisobutenes.
4. Acetylenes such as nonyne and dodecyne.

These unsaturated functional groups, in turn, can be substituted with nonhalogen-, substituents such as alkyl, carboxyl, amino, nitro, hydroxyl and alkoxy groups. Other coordination sites can be directly occupied by such groups.

The general formula for the preferred coordination II compounds is:



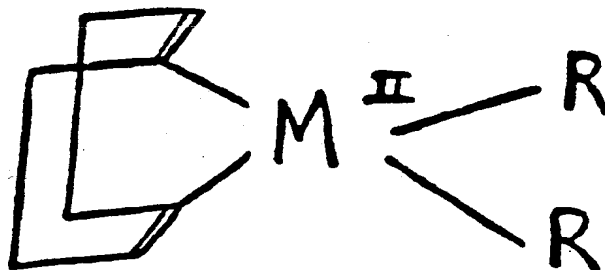
where  $M^{II}$  represents the platinum group metal, with

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a valence of +2, where A, B, D, and E are groups such as alkoxy, carboxyl, etc. described above, where  $(C = C)_x$  and  $(C = C)_y$  represent unsaturated functional groups coordinated with the platinum group metal, and where x and y are any integer.

Platinum group metals include platinum, palladium, rhodium, ruthenium, osmium, and iridium. Compounds including platinum, palladium and rhodium are preferred in the practice of this invention.

The most preferred platinum group coordination compounds are those represented by the following formula:



wherein M is a platinum group metal and R is benzyl, phenyl or nitrobenzyl.

The platinum group metal compound will be added to gasoline or diesel fuel in an amount effective to improve engine performance in terms of operating efficiency or emissions reduction. Typically, the compound will supply an amount of the metal within the range of from 0.01 to 1.0 parts of the platinum group metal per one million parts of gasoline (ppm w/v). A more preferred range is from 0.05 to 0.5 ppm, and most preferably, the platinum group metal will be supplied at a level of from 0.10 to 0.30 ppm on this same basis.

The fuel additive composition will preferably include a solvent which is miscible in the intended fuel, be it gasoline or diesel fuel. Certain of the

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solvents provide enhancements in the effectiveness of the platinum group metal compound and are preferred for this reason. Among the preferred solvents are oxygenated hydrocarbons, such as  
5 alcohols, heterocyclic oxygen compounds and ethers. Particularly preferred compounds are: 1 to 4 carbon alcohols, especially ethanol; tetrahydrofuran; and methyl tertiary butyl ether. Some of these compounds, as will be seen from the examples which  
10 follow, show especially strong enhancements with particular platinum group metal coordination compounds. Octyl nitrate functions well in diesel fuel additives.

The solvent will preferably be employed at a  
15 concentration of up to 5% of the fuel and typically greater than 0.25%. Solvent concentrations of from 0.25 to 2.5% are preferred, and are most preferably 1.0% or less, and in some cases show surprising improvements in additive performance when employed  
20 at these levels.

The preferred fuel additives will employ sufficient amounts of platinum group metal compounds and oxygenated solvent to provide a weight ratio of oxygen to platinum group metal of from 1,000:1 to  
25 100,000:1, preferably greater than 3,500:1. More preferred oxygen to platinum group metal weight ratios are from 5,000:1 to 35,000:1.

The fuel additive compositions can contain other additives such as detergents, antioxidants and  
30 octane improvers which are known as beneficial, but the use of such is not an essential feature of the invention.

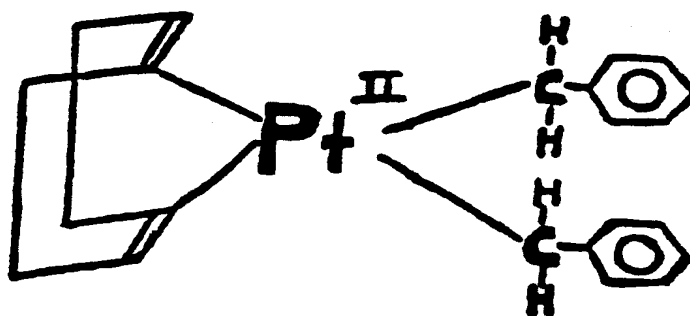
The following examples are presented for the purpose of further illustrating and explaining the  
35 present invention and the best mode for carrying it out, and are not to be taken as limiting.

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Example 1

Dibenzyl cyclooctadiene Pt II was used as a catalyst in unleaded gasoline supplied to an automobile engine.

- 5        Production of dibenzyl cyclooctadiene platinum II was accomplished by slurring 24.0 grams (0.064 mole) cyclooctadienyl Pt II dichloride in 200 milliliters of xylene. To the resultant mixture was added 0.5 mole benzyl magnesium chloride in diethyl ether (300 milliliters). The Grignard reaction was continued overnight, followed by hydrolysis with saturated ammonium sulfate solution in an ice bath. Following hydrolysis, the mixture was shaken vigorously and the layers were then allowed to separate. The organic phase was collected, dried over anhydrous sodium sulfate, and the residual diethyl ether was removed, leaving a solution of the product in xylene. This product has the structure:
- 10
- 15



- 20        The xylene solution of the platinum compound (0.17% by weight platinum) was admixed with other fuel additive components set forth in Table 1A below.

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A series of dynamometer tests were conducted, in which a 1984 Buick V-6 spark ignition engine was connected to and loaded by an eddy current dynamometer. The engine had the following specifications:

Engine Type	Buick 90°V-6
Bore and Stroke	3.800 x 3.400
Piston Displacement	231 cu. in.
Compression Ratio	8.0:1
Carburetor Type	2 BBL-ROCH
Air - Fuel/Ratio	14.7:1

Data gathered during comparative engine tests run on the Buick V-6 engine using unleaded Indolene gasoline with a platinum-based fuel additive formulation based on the following ingredients with a fuel employing all components of the formulation except the platinum compound:

---

<u>Table 1A</u>		Percent by Weight
	Xylene	58.6
	Methyl Tertiary Butyl Ether	40.5
	Detergent (Ethyl MPA-448)	0.9
	Platinum Coordination Compound as prepared above	0.012
This platinum compound has the following elemental breakdown:		
	Platinum	40.2%
	Carbon	54.4%
	Hydrogen	5.4%

---

The engine was run under steady conditions for about ninety (90) minutes per run at about 1300 rpm and



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was loaded to about 79 ft. lb. torque by a dynamometer to develop, on an average, 19.6 horsepower throughout each run.

During each of these runs, the time the engine took to consume a measured 900-milliliter quantity of gasoline with and without the platinum compound was recorded. For each run, such time readings were taken on three occasions and the time averaged. The product of the horsepower and average time (in minutes) to use 900 milliliters of fuel gave numbers representing work. The results are summarized below in Table 1B.

---

Table 1B

	<u>Baseline Run</u>	<u>Work</u>	<u>Run with Additive</u>	<u>Work</u>
15	1	176.4	1	186.2
	2	178.3	2	182.7
	3	176.1	3	184.1
	4	175.8	4	181.5
20	5	179.2	5	184.0
	6	178.8	6	189.5
	7	180.0	7	184.3
	8	177.1	8	183.0
	9	180.5	9	183.3
25	10	178.8	10	182.4
	11	179.7	11	183.5
	12	182.7		
	13	181.8		

---

The consumption times for 900 milliliters of gasoline containing 0.1 ppm of platinum supplied by the platinum compound were generally longer than the consumption times without the platinum compound. The average time with the platinum compound was 9.39

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minutes, and without was 9.11 minutes. This improvement of fuel consumption due to the platinum compound was 3.1%.

5 Fuel flow measurements showed a range of fuel efficiency gains of three percent (3%) to six percent (6%) with the platinum-based additive compared to the fuel additive formulation minus the platinum-based compound in a series of similar tests.

10

Example 2

The procedure of Example 1 was repeated, but this time employing 5% ethanol in addition to the fuel additive of Example 1 (at 0.2 ppm of platinum w/v). Baseline data was collected for 2 days and  
15 test data was noted on 12 days after an initial five days of operation employing the additive. The test engine was run at three rpm's (1300, 1800 and 2100) in sequence on each test day, all at a torque of 55 lb. ft. The data collected for fuel flow and  
20 hydrocarbon and carbon monoxide emissions are summarized below in Table 2.

Table 2

25	RPM	Fuel Flow (ml/sec)		Hydrocarbons (ppm w/v)		Carbon Monoxide (%)	
		Baseline	With Additive	Baseline	With Additive	Baseline	With Additive
	1300	1.12	1.07	210	135	1.79	0.62
	1800	1.82	1.76	169	113	1.05	0.40
30	2100	2.20	2.15	120	73	0.53	0.17

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Example 3

Additive testing was performed with a Buick engine having the specifications described in Example 1, mounted on a Superflow SF-901 water brake dynamometer. Superflow data collection capabilities included automatic measuring and recording of rpm torque, horsepower, as well as various temperatures, pressures, and flow rates.

Two of the engines spark plugs were fitted with Kistler spark plug pressure adapters (Model 640) and Kistler high impedance pressure transducers (Model 6001). An A.V.L. optical shaft encoder was mounted on the test engine which generated signals for bottom dead center and every half degree of crank angle.

Pressure and crank angle data were collected, stored and processed by a Columbia computer (Model 4220). Individual samples consisted of two pressure measurements for every half degree of shaft rotation over eighty firing cycles.

Each additive set forth in Table 3 below was tested in the following manner. A baseline test was performed without fuel treatment, followed by a test in which additive was present in the fuel, and finally the baseline test was repeated. Two pressure samples were collected during each test run. Tests were twelve and one half minutes in duration, with 20 minutes run time between tests to allow for conditioning or purging. The test engine was run at 2100 rpm and 55 lb. ft. of torque. Superflow data collection was sampled at ten second intervals. Standard deviation of horsepower was produced after each test in order to confirm engine

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stability and repeatability. Typical standard deviations averaged .06, for twelve and one half minutes of test engine run time.

5 The base fuel in each of the formulations tested was AMOCO unleaded regular gasoline having an octane rating of 87. In each case where ethanol (ETOH) or tetrahydrofuron (THF) was employed, its concentration was 0.25%. The DIBENZYL PT(II), referred to in the table was dibenzyl cyclooctadiene  
10 platinum II as prepared in Example 1; and, the NITROBENZYL PT(II) was similarly prepared but having nitrobenzyl in place of the two benzyl groups shown in the formula set forth in Example 1. Each of these platinum compounds, when employed, was used at  
15 a level sufficient to provide 0.15 ppm platinum, except where noted as being otherwise, e.g.,  $c = 0.1$ ,  $c = 0.2$ , or  $c = 0.3$  ppm. (The notation (all) indicates that this table summarizes data at all ethanol levels.)

20 For each test run which consisted of a baseline-additive-baseline sequence, the pressure measurements were plotted automatically as described above.

25 For each plot obtained, three parameters were studied:

1. Peak - The maximum pressure achieved in the cylinder during combustion.
2. Distance - A physical measurement of the horizontal distance between the top dead center axis and the peak of the pressure curve. Shorter distances between top dead center and peak pressure achieved indicate  
30 faster propagation of the flame front across the cylinder.

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3. MIP - The mean indicated pressure is the average pressure achieved after ignition at top dead center and is an indication of the total work release achieved by combusting the fuel.

5

In evaluating pressure curves with additive increases in peak pressure and MIP and decreases (shorter) distances were interpreted as a beneficial effect produced by the additive in terms of fuel utilization and useful work derived from combusting the fuel.

10

The nature of the effect of an additive treatment to fuel was studied by using the Analysis of Variance model otherwise known as (ANOVA). The assumptions that were made for this model have the following features:

15

1. There are two factor levels under study; baseline and treated conditions.
2. For each factor, the probability distribution of the data is normal.
3. All probability distributions of the factors have constant variance.
4. The mean for the data at each factor level may differ, reflecting the various effects of the treatment.

20

25

A statistical test can be performed to determine whether the means of the two factors are equal. If they are not, then further analysis is required.

- 20 -

This analysis involves the construction of an interval estimation of the mean response for a given factor, and comparison of mean responses for different factors. Statistical inferences can be made by using the interval estimation, i.e., it can be estimated with 80 or 90 percent confidence that the mean increase of the peak, dist or MIP are between the lower limit and the upper limit of the interval constructed. The interval estimation depends on the confidence level, the total number of points in the data as well as the variance of the difference of the two means. Thus conclusions can be made about the effect of the fuel treatment compared to nontreatment.

15

Table 3

	<u>Confidence Level</u>		<u>Lower Limit</u>	<u>Upper Limit</u>
			<u>ETOH vs BLANK</u>	
20	80%	Peak	0.75%	2.40%
		Dist	-0.39%	0.03%
		MIP	-0.43%	0.17%
	90%	Peak	0.42%	2.72%
		Dist	-0.47%	0.12%
25		MIP	-0.55%	0.29%
			<u>DIBENZYL PT(II) vs BLANK</u>	
	80%	Peak	-0.11%	1.05%
		Dist	0.10%	0.58%
		MIP	-1.23%	0.64%
30	90%	Peak	-0.34%	1.27%
		Dist	0.01%	0.67%
		MIP	-1.59%	1.01%

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		<u>Confidence</u> <u>Level</u>	<u>Lower Limit</u>	<u>Upper Limit</u>
<u>ETOH+DIBENZYL PT(II) vs BLANK</u>				
5	80%	Peak	3.50%	6.34%
		Dist	-0.93%	0.39%
		MIP	-0.22%	0.45%
	90%	Peak	2.94%	6.89%
		Dist	-1.19%	0.64%
		MIP	-0.35%	0.59%
<u>THF vs BLANK</u>				
10	80%	Peak	0.13%	1.05%
		Dist	-0.29%	0.11%
		MIP	-1.29%	-0.69%
	90%	Peak	-0.05%	1.23%
		Dist	-0.36%	0.19%
		MIP	-1.41%	-0.57%
<u>NITROBENZYL PT(II) vs BLANK</u>				
20	80%	Peak	-0.96%	0.76%
		Dist	-0.39%	0.28%
		MIP	-1.21%	-0.52%
	90%	Peak	-1.30%	1.09%
		Dist	-0.53%	0.41%
		MIP	-1.34%	-0.39%
<u>NITROBENZYL PT(II)+THF vs BLANK</u>				
25	80%	Peak	1.09%	1.99%
		Dist	-0.83%	-0.05%
		MIP	-0.91%	0.36%
	90%	Peak	0.92%	2.16%
		Dist	-0.98%	0.10%
		MIP	-1.16%	0.60%
30				

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		<u>Confidence</u> <u>Level</u>	<u>Lower Limit</u>	<u>Upper Limit</u>
<u>ETOH+DIBENZYL PT(II) vs ETOH (c=0.1)</u>				
5	80%	Peak	-3.22%	3.69%
		Dist	-1.12%	0.98%
		MIP	-1.15%	1.17%
	90%	Peak	-5.11%	5.59%
		Dist	-1.69%	1.56%
		MIP	-1.78%	1.80%
<u>ETOH+DIBENZYL PT(II) vs ETOH (c=0.2)</u>				
10	80%	Peak	-2.54%	4.45%
		Dist	-1.51%	0.53%
		MIP	-0.40%	0.10%
	90%	Peak	-4.46%	6.36%
		Dist	-2.07%	1.09%
		MIP	-0.54%	0.24%
<u>ETOH+DIBENZYL PT(II) vs ETOH (c=0.3)</u>				
20	80%	Peak	-2.49%	4.22%
		Dist	-1.51%	0.67%
		MIP	-0.23%	0.62%
	90%	Peak	-4.33%	6.05%
		Dist	-2.10%	1.26%
		MIP	-0.47%	0.86%
<u>ETOH+DIBENZYL PT(II) vs ETOH (ALL)</u>				
25	80%	Peak	0.56%	1.81%
		Dist	-0.47%	-0.04%
		MIP	0.12%	0.72%
	90%	Peak	0.36%	2.01%
		Dist	-0.54%	0.03%
		MIP	0.03%	0.81%
30	80%	Peak	0.56%	1.81%
		Dist	-0.47%	-0.04%
		MIP	0.12%	0.72%
	90%	Peak	0.36%	2.01%
		Dist	-0.54%	0.03%
		MIP	0.03%	0.81%



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Example 4

Following the test procedure of Example 3, (1) osmium (II) tris (acetylacetonate) and (2) bis (cyclopentadienyl) osmium (II) were tested against the base fuel with no additive as set forth in Example 3. The effect of each compound on peak, MIP and distance compared to base fuel was evaluated with the results as set forth in Table 4:

10

Table 4

<u>Compound Tested</u>	<u>% Change</u>		
	<u>Peak</u>	<u>MIP</u>	<u>Distance</u>
(1)	+0.125	-0.029	+0.079
(2)	+5.86	+0.847	0

15

Example 5

This example evaluates the performance of a diesel fuel additive according to the invention in reducing light duty diesel emissions and improving fuel economy. The fuel additive had the formulation set forth in Table 5A:

Table 5A

<u>Ingredient</u>	<u>Parts by Weight</u>
Diphenyl Cyclooctadiene Platinum II Coordination Compound	0.0170
Ethyl Dii-3 Octyl Nitrate	28.4
Ethyl EDA-2 Detergent	3.5
Xylene	2.6
Exxon LOPS Mineral Spirits	65.5

25

30

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Test Methodology

A 1984 Volvo GLE 760 diesel with five speed transmission and approximately 30,000 miles was selected as a test vehicle to provide data on a  
5 newer, but well broken-in, diesel engine.

The vehicle was driven to Scott Environmental Laboratories in Plumsteadville, Pennsylvania and allowed to stabilize for twelve hours prior to chassis dynamometer testing.

10 Baseline testing was conducted according to U.S. EPA Federal Test Procedures (urban cycle) and Highway Fuel Economy Test procedures. These procedures call for the dynamometer to be loaded to a prescribed setting and the vehicle to be driven  
15 through a series of acceleration, shifting, braking and stopping patterns as emissions and fuel economy data are collected. Data are collected over a series of runs and analyzed through a computer software program to arrive at a composite number for  
20 emissions and fuel economy performance.

Following baseline testing, the vehicle was treated with additive at the rate of seven ounces per twenty gallons of fuel and released to accumulate on-the-road mileage. The vehicle  
25 accumulated 1,600 miles before it was retested. Treatment was maintained during mileage accumulation through the use of pre-packaged additive introduced into the vehicle's fuel tank at each fuel fill-up to give an average concentration of platinum of about  
30 0.15 ppm. Treated fuel testing followed the same procedures as those for baseline testing.

The data is summarized in Table 5B.

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Table 5BFederal Emission Test Data

		<u>Baseline</u>	<u>Treated</u>	<u>% Increase</u>	<u>% Decrease</u>
5	CO <sub>2</sub>	343.44	303.98		11.49
	HC	0.14	0.17	21.43	
	CO	0.83	0.34		59.04
	NO <sub>x</sub>	1.00	0.48		52.00
	Particulate	0.32	0.30		6.25
10	MPG	25.69	29.07	13.16	

Highway Fuel Economy Test Data

		<u>Baseline</u>	<u>Treated</u>	<u>% Increase</u>	<u>% Decrease</u>
	CO <sub>2</sub>	231.88	199.55		13.94
15	HC	0.09	0.04		55.56
	CO	0.53	0.46		13.21
	NO <sub>x</sub>	0.61	0.33		45.90
	Particulate	--	--		--
	MPG	43.68	50.78	16.25	

20

Example 6

Two diesel passenger automobiles (a Peugeot and a Volkswagen Dasher) were fitted with on-board computers to record trip data and road tested over a

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200-mile highway route. In these demonstrations, route and load were held relatively constant, measuring fuel consumption with and without the additive of the invention. The road tests accumulated data for over 7,000 miles driven with untreated fuel and 6,400 miles for fuel treated with the additive detailed in Table 5A to give a platinum metal content of 0.15 ppm. From plots of the regression curves (mpg versus mph) a numerical integration was performed to determine the area under baseline and treated curves. The difference between the two areas was calculated in order to arrive at a percentage figure to describe the increase in mileage due to treatment with the fuel additive.

The results are summarized in Table 6.

---

<u>Table 6</u>			
20	<u>Peugeot</u>	Linear Regression	6.55% increase
		Quadratic Regression	8.49% increase
	<u>VW-Dasher</u>	Linear Regression	6.16% increase
		Quadratic Regression	6.78% increase

---

#### Example 7

25 Trials were conducted over a three-day period to evaluate the performance of the additive detailed in Table 5A in a Ruston GAPC medium speed diesel engine under closely controlled laboratory conditions. The engine was operated at a constant speed of 750 rpm within a power range of 35 to 85% of maximum continuous rating (MCR).

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Baseline fuel tests were performed on the first day, prior to additive introduction on the first and second days. On the first day, baseline fuel flow readings were recorded at power ratios of 35%, 50%, 5 62.5%, 75% and 85% MCR. Subsequently, additive was introduced in the ratio of one part additive to 250 parts fuel and the power reduced through the above range at hourly intervals. Fuel consumption was recorded at five-minute intervals. At the end of 10 the day's testing, the engine was shut down with additive remaining in the fuel system. The engine had no preconditioning or "seasoning" time on additive.

On the second say the engine was warmed up and 15 testing began using additive in a concentration of one part to 400. Engine power was progressively increased at hourly intervals through the same points as on the first day, with fuel consumption again recorded at five-minute intervals. An 20 additional baseline (untreated fuel) test was run on the third day.

Analysis of the data collected on the first day presented in Table 7A indicate a reduction in fuel consumption of 3.1% to 5.3% when using the additive. 25 Treated data acquisition progressed from high load (420 kw) to low load (220 kw). Absolute reduction in fuel consumption is noted to improve from no reduction initially (first treated data point) to a 5.3% reduction at the end of the sequence.

30 Data presented in Table 7B represent a comparison of treated data collected on the second day versus the baseline data of the first day. Percentage reduction in fuel consumption ranged from 3.3% to 4.0% when using the additive. Absolute 35 reduction in fuel consumption is noted to improve from 2.4 kg/hr to 3.3 kg/hr, which follows the trend

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towards increased time of treatment during the progression from low load operation (275 kw) to high load operation (475 kw) on the second day.

5 Data collected on the third day (not shown) for untreated operation appear identical to those for treated operation the second day. This is probably the result of a residual effect of additive deposited on cylinder parts and lube oil components during treatment.

10

Table 7A

Comparison of Baseline Fuel Consumption vs.  
Treated Fuel Consumption at Indicated Loads  
 (First Day Data)

15

Power (kw)	Treated Fuel Consumption (kg/hr)	Untreated Fuel Consumption (kg/hr)	Reduction in Fuel Consumption with Additive	
			(kg/hr)	Reduction %
20 420	86.8	86.8	--	--
345	71.5	73.8	2.3	3.1
280	58.7	61.3	2.6	4.2
220	46.5	49.1	2.6	5.3

25

Table 7B

Comparison of Baseline Fuel Consumption vs.  
Treated Fuel Consumption at Indicated Loads  
 (Second Day Data)

30

Power (kw)	Treated Fuel Consumption (kg/hr)	Untreated Fuel Consumption (kg/hr)	Reduction in Fuel Consumption with Additive	
			(kg/hr)	Reduction %
35 275	57.6	60.0	2.4	4.0
347	71.2	74.2	3.0	4.0
410	84.0	87.1	3.1	3.6
475	95.9	99.2	3.3	3.3

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Example 8

This test evaluates the effect of the additive detailed in Table 5A on the fuel economy and horsepower output of a commercially-operated, diesel-powered truck tractor.

On the first day of testing, baseline (no additive) chassis dynamometer tests were conducted. The vehicle tested was a tandem tractor powered by a Cummins NHC-250 engine. The vehicle was supplied by an independent owner-operator and was normally used in highway construction hauling. The engine had accumulated 8,000 miles since rebuild.

Following baseline testing and treatment at a rate of one gallon of additive to four hundred gallons of fuel, the vehicle was released to accumulate approximately 1000 miles of over-the-road treated data before being retested on the chassis dynamometer.

During over-the-road mileage accumulation, treatment was maintained by the driver according to a treatment schedule which provided for a 1:400 dosage rate. Product was supplied in one-gallon containers along with a graduated beaker for accurate measurement. Daily record sheets were completed by the driver to record miles driven and fuel and additive consumed.

During dynamometer testing, the tractor was secured to a Clayton water-brake dynamometer and run for four minute intervals at settings of 2100 rpm and full power, 2000 rpm and full power and 1900 rpm and full power. Readings were taken every minute from the dynamometer's gauges, recording the actual rear wheel horsepower. A separate tachometer was installed in the cab. The one in the tractor was

- 30 -

found to "bounce". The speed and horsepower balance were maintained at the rear wheels from the cab. Simultaneously, fuel measurements were taken at the same intervals. A thirty gallon drum of fuel was  
5 placed on an accurate digital scale and the reduction in the weight of the fuel was recorded. Recirculation was returned to the drum to measure only that fuel consumed. The combined rear wheel horsepower was found to be equal to factory  
10 specifications, i.e., 70% of rated 250 horsepower, equal to 175. Prior to testing the engine was checked by the manufacturer to be sure that the fuel flow and fuel pressure agreed with the manufacturer's specifications for the fuel pump.

15 Two test runs were conducted on each test date to assure the repeatability of results. Each test consisted of three minutes of stabilized run time at each of the three rpm settings with one minute in between to allow for stabilization and transition to  
20 the next rpm level.

The averages of three readings for each rpm setting are summarized in Table 8A for untreated and treated data. Table 8A provides a comparison of horsepower (output) versus fuel flow (input) at a  
25 given engine rpm for untreated and treated data. Horsepower increases following additive treatment averaged 2.6% to 5.2% improvement over baseline.

Table 8B provides a comparison of actual horsepower increase using the additive versus  
30 untreated data. Actual horsepower increases ranged from 4.5 hp to 9.0 hp following additive treatment.



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Table 8A  
Horsepower and Fuel Flow Data  
at Indicated RPM

	----UNTREATED----			-----TREATED-----		
	Run 1	Run 2	Avg	Run 1	Run 2	Avg
5 (2100) hp	170	174	172	181	181	181
Fuel Flow (lb/min)	1.6	1.6	1.6	1.6	1.6	1.6
(2000) hp	172	173	172.5	180	180	180
10 Fuel Flow (lb/min)	1.5	1.6	1.55	1.5	1.6	1.55
(1900) hp	173	173	173	177	178	177.5
Fuel Flow (lb/min)	1.5	1.5	1.5	1.5	1.5	1.5

15

Table 8B

Actual HP Improvement Resulting from  
Additive Treatment

	<u>RPM</u>	<u>Untreated</u> (2 run avg)	<u>Treated</u> (2 run avg)	<u>HP Change</u>
20	2100	172	181	9.0
	2000	172.5	180	7.5
	1900	173	177.5	4.5
Average HP Improvement:				7.0

25 Fuel flow remained nearly constant during the tests, while actual horsepower measured by the dynamometer increased for the treated runs. Actual horsepower improvement averaged 7.0 hp for the treated runs over the three rpm settings. This  
30 corresponds to a 4.0% increase in horsepower over baseline horsepower.

The dynamometer was not equipped to run treated tests at equivalent baseline horsepower in order to

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monitor decrease in fuel flow; however, a calculation of brake specific fuel consumption (BSFC) is one means of recording the fact that more work is produced per unit of fuel when using the additive. Therefore, if power requirements were held constant, less fuel would be consumed when using the additive. The data provided in Table 8C represent BSFC, pounds of fuel consumed per horsepower-hour for untreated and treated data. The improvement using additive ranged from 2.5% to 5.0%.

Emissions measurements were not quantified during these tests; however, a reduction in visible smoke emissions was observed when running on treated fuel at start-up, idle and loaded conditions.

15

---

Table 8C

Brake Specific Fuel Consumption  
vs. RPM  
 (BSFC in lb per hp-hr)

<u>RPM</u>	<u>-----UNTREATED-----</u>			<u>-----TREATED-----</u>			<u>Improvement</u>
	<u>Run 1</u>	<u>Run 2</u>	<u>Avg</u>	<u>Run 1</u>	<u>Run 2</u>	<u>Avg</u>	
2100	0.564	0.551	0.558	0.530	0.530	0.530	5.0%
2000	0.523	0.554	0.539	0.500	0.533	0.517	4.1%
1900	0.520	0.520	0.520	0.508	0.505	0.507	2.5%

25

Example 9

This test evaluates the effectiveness of the diesel fuel additive set forth in Table 5A in a high elevation test on large tractors presently used for hauling. Two tractors were selected -- a new Kenworth with a 400 horsepower Caterpillar engine

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(31,000 total miles) and a Kenworth with a 475 horsepower Cummins twin-turbo engine (172,000 total miles).

Testing Method (Over-the-Road)

5 Baseline data from previous months' records was listed indicating date, miles driven, gallons of fuel used and then miles per gallon was calculated. The two selected vehicles were then tested on a chassis dynamometer for baseline determination (see  
10 Testing Method-Chassis Dynamometer). After the dynamometer tests, the tractors were treated with the fuel additive and returned to their commercial routes. The next two months (treated data) were then listed and compared to the original (untreated)  
15 baseline data.

Testing Method (Chassis Dynamometer)

Both Kenworth tractors were tested on an Ostradyne Model U130TT chassis dynamometer. The specifications of the unit are horsepower limit 500,  
20 torque limit 1500 lb. ft., maximum rear wheel speed was 60 mph.

The tractors were driven onto the dynamometer such that the rear driving wheels of the tractor turned a set of rollers. These rollers are  
25 connected to a braking system. The force required on the turning rollers to load the tractor's rear driving wheels is indicated on various meters located on the dynamometer's control panel. The meters consisted of horsepower, torque, speed  
30 (calibrated in miles per hour) and also a separate panel with controls to adjust for barometric pressure, humidity, etc.

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The test consisted of selecting three basic rpm's in the upper scale of the tractor's capability. The tractor was then fully loaded maintaining the specific rpm and the meters on the dynamometer were recorded every minute for 5 minutes.

Fuel flow was measured by filling a 20 gallon pail with diesel fuel from the tractor's saddle tanks. The 20 gallon pail was placed on an accurate electronic scale. During the 5 minute load tests, minute readings were taken from the scale so an accurate accounting of the fuel usage in pounds of fuel per minute was recorded.

#### Data Evaluation (Over-the-Road)

The over-the-road data for both tractors is summarized in Tables 9A and 9B. Both tractors showed improvements in excess of 5.6% in MPG while under treatment; with a discernable trend towards continued improvement with time under treatment.

Table 9A

#### Kenworth-Caterpillar

<u>Baseline</u>		<u>Treated</u>	
<u>Day</u>	<u>MPG</u>	<u>Day</u>	<u>MPG</u>
25	1 4.13	1 4.60	
	2 4.15	2 4.63	
	3 4.11	3 4.86	
	4 4.20	4 4.67	
	5 3.84	5 4.95	
30	6 4.74	6 5.02	
	7 4.15		
	8 4.19		
-----			
	N: 8.00	N: 6.00	
35	AVG: 4.189	AVG: 4.788	
	STD: 0.23	STD: 0.16	

Improvement with Treatment = 0.599 mpg or 14.300%

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Table 9B

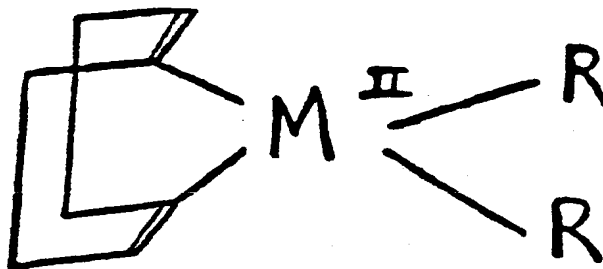
<u>Baseline</u>		<u>Treated</u>	
<u>Day</u>	<u>MPG</u>	<u>Day</u>	<u>MPG</u>
5	1	1	4.87
	2	2	4.64
	3	3	4.87
		4	5.20
-----			
10	N:	N:	4.00
	AVG:	AVG:	4.895
	STD:	STD:	0.200
Improvement with Treatment = 0.285 mpg or 6.18%			

15       The above description is for the purpose of  
teaching the person of ordinary skill in the art how  
to practice the present invention and is not  
intended to detail all those obvious modifications  
and variations of it which will become apparent to  
20 the skilled worker upon reading the description. It  
is intended, however, that all such obvious  
modifications and variations be included within the  
scope of the present invention which is defined by  
the following claims.

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CLAIMS

1. A fuel additive composition for a fuel selected from the group consisting of gasoline and diesel fuel comprising a solution of a fuel-soluble platinum group metal coordination compound of the formula:



wherein M is a platinum group metal and R is phenyl, benzyl, or nitrobenzyl, dissolved in an oxygenated hydrocarbon solvent, in amounts effective to supply platinum group metal and oxygen at a weight ratio of oxygen to metal within the range of from 1,000:1 to 100,000:1

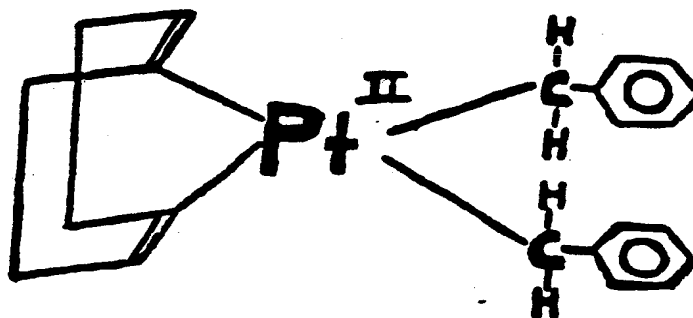
2. A composition according to Claim 1 wherein the platinum group metal comprises platinum.
3. A composition according to Claim 1 wherein the oxygenated hydrocarbon comprises ethanol, tetrahydrofuran, methyl tertiary butyl ether or combinations of these.
4. A composition according to Claim 3 wherein R comprises benzyl and the solvent comprises ethanol.

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5. A composition according to Claim 3 wherein R comprises nitrobenzyl and the solvent comprises tetrahydrofuran.

6.. A composition according to Claim 3 wherein the  
5 solvent comprises methyl tertiary butyl ether.

7. A gasoline additive composition comprising a gasoline miscible solution of a platinum coordination compound of the formula:



10 and ethanol or tetrahydrofuran in amounts effective to supply platinum and oxygen at a weight ratio of oxygen to platinum of from 3,500:1 to 100,000:1.

8. A fuel additive composition comprising a solution of a fuel-soluble platinum group metal compound in a solvent miscible in the fuel, the  
15 platinum group metal being present in an amount sufficient to supply from 0.01 to 1.0 parts per million of the platinum group metal when added to a predetermined amount of fuel.

9. A composition according to Claim 8 wherein the  
20 solvent comprises an oxygenated hydrocarbon.

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10. A composition according to Claim 9 wherein the oxygenated hydrocarbon comprises an alcohol having from 1 to 4 carbon atoms.
11. A composition according to Claim 10 wherein the  
5 alcohol comprises ethanol.
12. A composition according to Claim 11 wherein the ethanol is present in an amount sufficient to supply up (from 0.25) to 5.0 parts of ethanol per 100 parts of gasoline.
- 10 13. A composition according to Claim 12 wherein the platinum group metal compound and the ethanol are supplied in amounts effective to supply platinum group metal and oxygen at a weight ratio of oxygen to metal of from 1,000:1 to 100,000:1.
- 15 14. A composition according to Claim 13 wherein the weight ratio of oxygen from the ethanol to platinum group metal is within the range of from 5,000:1 to 35,000:1.
- 20 15. A composition according to Claim 8 wherein the platinum group metal compound is a platinum group metal coordination compound comprising a platinum group metal having a +2 or +4 coordination state with at least one coordination site in the compound being occupied by a functional group containing at  
25 least one unsaturated carbon-to-carbon bond with an olefinic, acetylenic or aromatic pi bond configuration.



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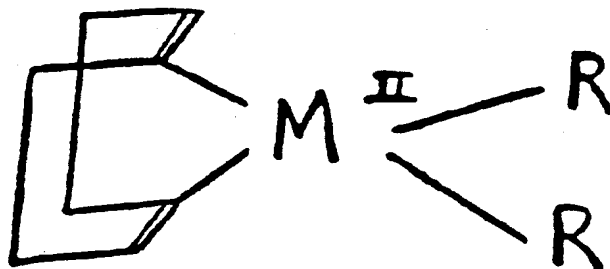
16. A composition according to Claim 15 wherein two or more coordination sites are occupied by functional groups containing at least one unsaturated carbon-to-carbon bond with an olefinic, acetylenic or aromatic pi bond configuration.
17. A composition according to Claim 15 wherein the unsaturated bond-containing functional groups are further substituted with nonhalogen-containing constituents selected from the group consisting of alkyl, carboxyl, amino, nitro, hydroxyl and alkoxyl groups.
18. A composition according to Claim 15 wherein other coordination sites are directly occupied by nonhalogen-containing substituents selected from the group consisting of alkyl, carboxyl, amino, nitro, hydroxyl and alkoxyl groups.
19. A composition according to Claim 15 wherein the unsaturated bond-containing functional groups are selected from the group consisting of aromatic, cycloaliphatic, olefinic and acetylenic groups.
20. A composition according to Claim 15 wherein the platinum group metal is platinum, palladium, or rhodium or mixtures thereof.
21. A composition according to Claim 15 wherein one of the functional groups is a cycloalkadiene.

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22. A gasoline composition comprising gasoline and an additive composition dissolved therein, said additive composition comprising a gasoline-soluble platinum group metal compound in an amount effective to supply from 0.01 to 1.0 parts per million of the platinum group metal per part of gasoline.
23. A gasoline composition according to Claim 22 which further comprises a gasoline-soluble solvent for said platinum group metal compound.
24. A gasoline composition according to Claim 23 wherein the solvent is an oxygenated hydrocarbon.
25. A gasoline composition according to Claim 23 wherein the platinum group metal and the oxygen from the solvent are present at an oxygen to metal weight ratio of from 1,000:1 to 100,000:1.
26. A gasoline composition according to Claim 24 wherein the solvent is an alcohol having from one to four carbon atoms.
27. A gasoline composition according to Claim 26 wherein the solvent is ethanol and is employed at a level of from 0.25 to about 5 percent of the weight of the gasoline composition.
28. A gasoline composition according to Claim 27 wherein the ethanol is employed at a level up to 1% of the composition and the platinum group metal is present at a level of from 0.05 to 0.5 parts per million parts gasoline.

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29. A gasoline composition according to Claim 22 wherein the platinum group metal compound comprises a gasoline-soluble platinum group metal coordination compound of the formula:



5 wherein M is a platinum group metal and R is phenyl, benzyl or nitrobenzyl.

30. A gasoline composition according to Claim 29 wherein M is platinum.

31. A gasoline composition according to Claim 30  
10 which further includes a solvent comprising ethanol, tetrahydrofuran, methyl tertiary butyl ether, or combinations of these.

32. A gasoline composition according to Claim 31  
15 wherein R comprises benzyl and the solvent comprises ethanol.

33. A gasoline composition according to Claim 31 wherein R comprises nitrobenzyl and the solvent comprises tetrahydrofuran.

34. A gasoline composition according to Claim 31  
20 wherein the solvent comprises methyl tertiary butyl ether.

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35. A gasoline composition comprising gasoline and dissolved therein from 0.01 to 1.0 parts per million parts gasoline of a platinum group metal coordination compound comprising a platinum group metal having a +2 or +4 coordination state with at least one coordination site in the compound being occupied by a functional group containing at least one unsaturated carbon-to-carbon bond with an olefinic, acetylenic or aromatic pi bond configuration.

36. A composition according to Claim 35 wherein two or more coordination sites are occupied by functional groups containing at least one unsaturated carbon-to-carbon bond with an olefinic, acetylenic or aromatic pi bond configuration.

37. A composition according to Claim 35 wherein the unsaturated bond-containing functional groups are further substituted with nonhalogen-containing constituents selected from the group consisting of alkyl, carboxyl, amino, nitro, hydroxyl and alkoxyl groups.

38. A composition according to Claim 35 wherein other coordination sites are directly occupied by nonhalogen-containing substituents selected from the group consisting of alkyl, carboxyl, amino, nitro, hydroxyl and alkoxyl groups.

39. A composition according to Claim 35 wherein the unsaturated bond-containing functional groups are selected from the group consisting of aromatic, cyclodienic, olefinic and acetylenic groups.

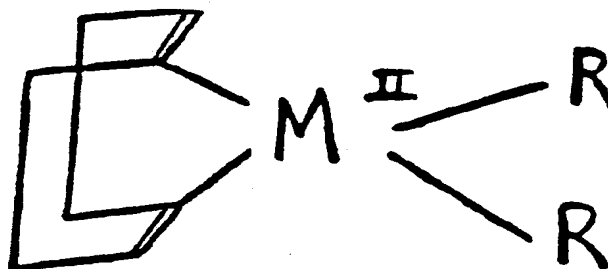
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40. A composition according to Claim 35 wherein the platinum group metal is platinum, palladium, or rhodium or mixtures thereof.
41. A composition according to Claim 35 wherein at least one of the functional groups is a cycloalkadiene.
42. A diesel fuel composition comprising diesel fuel and an additive composition dissolved therein, said additive composition comprising a fuel-soluble platinum group metal compound in an amount effective to supply from 0.01 to 1.0 parts per million of the platinum group metal per part of fuel.
43. A composition according to Claim 42 which further comprises a diesel fuel-soluble solvent for said platinum group metal compound.
44. A composition according to Claim 43 wherein the solvent is an oxygenated hydrocarbon.
45. A composition according to Claim 43 wherein the platinum group metal and the oxygen from the solvent are present at an oxygen to metal weight ratio of from 1,000:1 to 100,000:1.
46. A composition according to Claim 44 wherein the solvent is an alcohol having from one to four carbon atoms.
47. A composition according to Claim 44 wherein the solvent is octyl nitrate.

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48. A composition according to Claim 46 wherein the solvent is ethanol and is employed at a level of from 0.25 to about 5 percent of the weight of the composition.

- 5 49. A composition according to Claim 48 wherein the ethanol is employed at a level up to 1% of the composition and the platinum group metal is present at a level of from 0.05 to 0.5 parts per million parts diesel fuel.
- 10 50. A composition according to Claim 42 wherein the platinum group metal compound comprises a fuel-soluble platinum group metal coordination compound of the formula:



wherein  $M$  is a platinum group metal and  $R$  is phenyl,  
15 benzyl or nitrobenzyl.

51. A composition according to Claim 50 wherein  $M$  is platinum.

52. A composition according to Claim 51 which further includes a solvent comprising ethanol, octyl  
20 nitrate, tetrahydrofuran, methyl tertiary butyl ether, or combinations of these.

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53. A composition according to Claim 52 wherein R comprises benzyl and the solvent comprises ethanol.
54. A composition according to Claim 52 wherein R comprises phenyl and the solvent comprises octyl  
5 nitrate.
55. A composition according to Claim 52 wherein the solvent comprises methyl tertiary butyl ether.
56. A diesel fuel composition comprising diesel  
fuel and dissolved therein from 0.01 to 1.0 parts  
10 per million parts diesel fuel of a platinum group  
metal coordination compound comprising a platinum  
group metal having a +2 or +4 coordination state  
with at least one coordination site in the compound  
being occupied by a functional group containing at  
15 least one unsaturated carbon-to-carbon bond with an  
olefinic, acetylenic or aromatic pi bond  
configuration.
57. A composition according to Claim 56 wherein two  
or more coordination sites are occupied by  
20 functional groups containing at least one  
unsaturated carbon-to-carbon bond with an olefinic,  
acetylenic or aromatic pi bond configuration.
58. A composition according to Claim 56 wherein the  
unsaturated bond-containing functional groups are  
25 further substituted with nonhalogen-containing  
constituents selected from the group consisting of  
alkyl, carboxyl, amino, nitro, hydroxyl and alkoxyl  
groups.

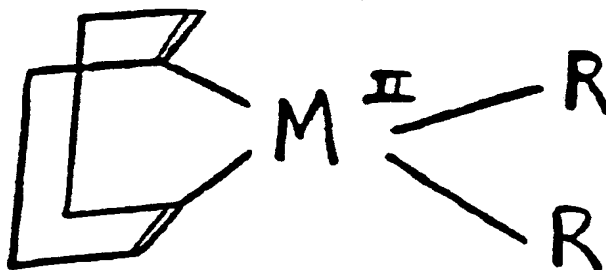
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59. A composition according to Claim 56 wherein other coordination sites are directly occupied by nonhalogen-containing substituents selected from the group consisting of alkyl, carboxyl, amino, nitro, hydroxyl and alkoxyl groups.
60. A composition according to Claim 56 wherein the unsaturated bond-containing functional groups are selected from the group consisting of aromatic, cycloclodienic, olefinic and acetylenic groups.
61. A composition according to Claim 56 wherein the platinum group metal is platinum, palladium, or rhodium or mixtures thereof.
62. A composition according to Claim 56 wherein at least one of the functional groups is a cyclo-alkadiene.
63. A method of increasing the utilizable energy of gasoline or diesel fuel for powering internal combustion engines, comprising admixing with said gasoline or diesel fuel a fuel additive composition comprising a fuel-soluble platinum group metal compound in an amount effective to supply from 0.01 to 1.0 parts per million parts of the platinum group metal per part of fuel.
64. A method according to Claim 63 wherein said fuel additive composition further comprises a fuel-soluble solvent for said platinum group metal compound.



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65. A method according to Claim 63 wherein the platinum group metal and the solvent are present in amounts sufficient to supply oxygen and metal at a weight ratio of from 1,000:1 to 100,000:1.
- 5 66. A method according to Claim 64 wherein the solvent is an alcohol having from one to four carbon atoms.
67. A method according to Claim 66 wherein the solvent is ethanol and is employed at a level of  
10 from 0.25 to about 5 percent of the weight of the fuel.
68. A method according to Claim 67 wherein the ethanol is employed at a level up to 1% of the composition and the platinum group metal is present  
15 at a level of from 0.05 to 0.5 parts per million parts fuel.
69. A method according to Claim 42 wherein the platinum group metal compound comprises a fuel-soluble platinum group metal coordination  
20 compound of the formula:



wherein M is a platinum group metal and R is phenyl, benzyl or nitrobenzyl.

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70. A method according to Claim 69 wherein M is platinum.

71. A method according to Claim 70 which further includes a solvent comprising ethanol, tetra-  
5 hydrofuran, methyl tertiary butyl ether, or combinations of these.

72. A method according to Claim 71 wherein R comprises benzyl and the solvent comprises ethanol.

73. A method according to Claim 72 wherein R  
10 comprises nitrobenzyl and the solvent comprises tetrahydrofuran.

74. A method according to Claim 72 wherein the solvent comprises methyl tertiary butyl ether.

75. A method for increasing the efficiency of a  
15 gasoline or diesel engine comprising dissolving in a fuel selected from the group comprising of gasoline and diesel fuel, from 0.01 to 1.0 parts per million parts gasoline of a platinum group metal coordination compound comprising a platinum group  
20 metal having a +2 or +4 coordination state with at least one coordination site in the compound being occupied by a functional group containing at least one unsaturated carbon-to-carbon bond with an olefinic, acetylenic or aromatic pi bond  
25 configuration, and operating said engine employing the fuel with the dissolved platinum group metal compound.

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76. A method according to Claim 75 wherein, preferably, two or more coordination sites of the platinum group metal compound are occupied by functional groups containing at least one  
5 unsaturated carbon-to-carbon bond with an olefinic, acetylenic or aromatic pi bond configuration.

77. A method according to Claim 75 wherein the unsaturated bond-containing functional groups are further substituted with nonhalogen-containing  
10 constituents selected from the group consisting of alkyl, carboxyl, amino, nitro, hydroxyl and alkoxyl groups.

78. A method according to Claim 75 wherein other coordination sites are directly occupied by  
15 nonhalogen-containing substituents selected from the group consisting of alkyl, carboxyl, amino, nitro, hydroxyl and alkoxyl groups.

79. A method according to Claim 75 wherein the unsaturated bond-containing functional groups are  
20 selected from the group consisting of aromatic, cycloclodienic, olefinic and acetylenic groups.

80. A method according to Claim 75 wherein the platinum group metal is platinum, palladium or rhodium or mixtures thereof.

25 81. A method according to Claim 76 wherein at least one of the functional groups is a cycloalkadiene.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US85/02387

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>3</sup> According to International Patent Classification (IPC) or to both National Classification and IPC Int. Class <sup>4</sup> C07F 3/00; C10L 1/08; C10L 1/12; C10L 1/14 U.S. Class 260/429R; 44/57; 44/67; 44/68						
<b>II. FIELDS SEARCHED</b> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched <sup>4</sup></div> <table style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%; border-bottom: 1px solid black;">Classification System</th> <th style="border-bottom: 1px solid black;">Classification Symbols</th> </tr> <tr> <td style="border-right: 1px solid black; padding: 5px;">U.S.</td> <td style="padding: 5px;">44/57, 67, 68; 260/429R</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>5</sup></div>			Classification System	Classification Symbols	U.S.	44/57, 67, 68; 260/429R
Classification System	Classification Symbols					
U.S.	44/57, 67, 68; 260/429R					
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>						
Category <sup>6</sup>	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>				
Y	U.S., A, 2,875,223 Published, 24 February 1959, Pedersen et al.	1-81				
Y	U.S., A, 4,207,078 Published, 10 June 1980, Sweeney et al.	1-81				
Y	N, U. Belluco, 'Organometallic and Coordination Chemistry of Platinum', Published 1974, by Academic Press (N.Y.), see pages 221,222,226,232,295-297,441,449,454 and 455.	1-81				
Y	N, G. Deganello, 'Transition Metal Complexes of Cyclic Polyolefins', Published 1979, by Academic Press (N.Y.), see pages 97-100,102,277,278,281 to 283,288,289-291.	1-81				
Y	N, R. Dickson, 'Organometallic Chemistry of Rhodium and Iridium', Published 1983, by Academic Press (N.Y.), pages 167-169,178-180,198-200,220-226,248,258-260,264,271, and 277.	1-81				
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>16</sup> * Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>						
<b>IV. CERTIFICATION</b>						
Date of the Actual Completion of the International Search <sup>2</sup> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">10 February 1986</div>		Date of Mailing of this International Search Report <sup>2</sup> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">14 FEB 1986</div>				
International Searching Authority <sup>1</sup> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">ISA/US</div>		Signature of Authorized Officer <sup>19</sup> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">          Margaret B. Medley       </div>				

## III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No <sup>18</sup>
Y	N, P. Maitlis, 'The Organic Chemistry of Palladium', Published 1971, by Academic Press (N.Y.), see pages 68,70,76,77,83, 93,102,103,136,158,165,202-204,228,242,249 257 and 258.	1-81
A	N, Chemical Abstracts, Volume 76, issued 1972, see page 433, column 1, the abstract no. 112565P, Johnson, B. F. G. et al 1972; and see pages 499, column 2 the abstract no. 113355g, Hughes, R. P. et al (1972)	1-81
A	N, Chemical Abstracts, Volume 82, issued 1975, see page 384, column 1, the abstract no. 4403z, Zakharkin, L. I. et al (1974)	1-81
A	N, Chemical Abstracts, Volume 97, issued 1982, see page 629, column 2, the abstract no. 110175w, Lutsenko, Z. L. et al (1982) and see page 630, column 1 and 2, the abstract no. 110181v Fuchita, S. et al (1981)	1-81